Operating behaviour of a reactor with exothermic reaction

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ABSTRACT
The reactors with exothermic reactions exhibit a complex coupling between temperature and reaction rate in the reactor. The reactor temperature has to be controlled to avoid runaways of the system. Many studies have been carried out to study the parameters influencing changes in the reactor temperature as well as the consequences of the temperature for the working conditions of the reactor. An analytical solution to the problem is studied to find approximate relations between the working conditions and temperature. Approximate equations for the calculation of the limiting working conditions are presented.

NOMENCLATURE

\( C \) : mole concentration, mol/m\(^3\)
\( \dot{M} \) : mass flow rate, m/s
\( \dot{Q} \) : heat transfer rate, W
\( R \) : gas constant, J/(kmol K)
\( T \) : temperature, K
\( V \) : volume, m\(^3\)
\( W \) : molecular weight, kg/mole
\( Y \) : mass fraction,
\( c_p \) : heat capacity, J/(g K)
\( h \) : enthalpy, J/kg
\( k \) : reaction rate, m\(^3\)/(mol s K\(^n\)) (for reaction with two reactants)

Greek Symbols
\( \gamma \) : stoichiometric factor the fuel-air-ratio
\( \omega \) : production rate

Subscripts
\( A \) : species
\( F \) : fuel
\( Ox \) : oxidator
\( P \) : product
\( 0 \) : initial condition
\( ad \) : adiabatic

Superscripts
\( 0 \) : creation
\' : output

INTRODUCTION
The analysis of chemical reactors with exothermic reactions is not only important for the practical cases, such as describing the combustion in a gas turbine combustion chamber but also as an example for a regenerative or self-referential system. In such a regenerative system the description of the operating behaviours and working temperatures has its difficulty in the fact that the reaction rate in the reactor depends in a non-linear way from the temperature which at the same time depends on the reaction rate.

The balance between heat release and heat removal will be analysed as well as the influence of different parameters on this balance. The consequences for the working conditions of the reactor will be analysed qualitatively.

PROBLEM STATEMENT
An overriding design consideration for a reactor with exothermic reactions lies in the controlled temperature development in the reactor.

The temperature should be high enough for the reaction to start but at the same time after the reaction not so high that the temperature and pressure in the reactor overcome its endurance. An excessive temperature excursion may adversely affect the conversion of the exothermic equilibrium reaction and the selectivity of the reaction process. In the case of catalytic reaction it could affect the catalyst activity and durability and even the reactor safety. [1]

The main reason for the research in the past 30 years remains in the sensitivity of the reactor temperature to a change in the reaction conditions. Different parameters have been analysed. For example a slight change in the inlet temperature can lead to a situation in which the reactor temperature runs away, resulting in explosion in some cases. This sensitivity problem therefore represents a constraint on the range of operating conditions, which in turn limits the maximum conversion through the exothermic reaction that can be achieved safely. [2]

Knowledge of the circumstances leading to thermal runaway and knowledge of the process chemistry are essential factors for a safe operation of chemical reactors.

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LITERATURE SURVEY
Different researches have been made to analyse the influencing parameters on the reactor temperature.
N.S. Jayakumar [3] investigates the existence and effect of parametric sensitivity with respect to the input parameters in batch chemical reactors in a certain range of operating conditions with parametric sensitivity. The analysed parameters were the cooling water flow rate, cooling water feed temperature and wall capacitance. Parametric sensitivity was observed for small changes in cooling water flow rate and cooling water feed temperature, for which the reactor temperature changed considerably. On the contrary no sensitivity for changes in the wall capacitance was found in parametric sensitive conditions, which showed that the presence of extraneous wall capacitance tends to stabilize the reactor.

Variable cross-section reactors for highly exothermic reactions were studied from L. M. Akella [2], showing that by properly varying the reactor cross section along its length a better reactor performance can be achieved. This would decrease the equipment costs (decreased size) and operating costs (decreased pressure drop) replacing the usual practice of uniformly decreasing the tube diameter for a better heat removal with the consequence of an increased tube length for a given desired conversion. This is possible as under a typical runaway situation, only a fraction of the reactor length around the hot spot is subjected to extreme temperatures. Furthermore an additional degree of freedom is offered, as it allows a higher conversion or a broader safe operating range at the same conversion.

PROJECT DESCRIPTION
For a better understanding of the heat balance and working behaviour of the reactor a simplified analytical analysis is made in the following lines with help of [4].
The reactor is considered as an idealised well stirred reactor with exothermic reaction. In this case the outflow conditions will be the same as the conditions in the reactor (see. Fig.1).

Species and energy balance
A steady state can only be achieved if inflow and outflow fluxes and enthalpies are in balance with the released enthalpy of the chemical reaction.
The species balance for a well stirred reactor can be written as in eq. 1.

\[-\dot{M} \cdot Y_A + \dot{M} \cdot Y'_A = \omega_A \cdot W_A \cdot V \quad A = 1 \ldots N \]  

(1)

The energy balance for an isobaric reactor can be expressed as follows, with \( \dot{Q}_K \) representing the heat losses to the surroundings.

\[-\dot{M} \sum_{A=1}^{N} Y_A \cdot h_A + \dot{M} \sum_{A=1}^{N} Y'_A \cdot h_A' + \dot{Q}_K = 0 \]  

(2)

For an adiabatic reactor \( \dot{Q}_K = 0 \) and with \( h_A(T) = h_A^0 + \int_{T_{ref}}^{T} c_{p,A}(T) dT \), one can write:

\[-\dot{M} \sum_{A=1}^{N} \left[ Y'_A \int_{T_{ref}}^{T} c_{p,A}(T) dT - Y_A \int_{T_{ref}}^{T} c_{p,A}(T) dT \right] = \dot{M} \sum_{A=1}^{N} (Y'_A - Y_A) \cdot h_A^0 \]  

(3)

On the left side of eq. 3 we see the inflow and outflow fluxes with their temperature dependent enthalpy and on the right side we see the terms representing the heat released through the chemical reaction.

With equations (1) and (3) we have a system of N+1 equations and N+1 unknowns for \( Y'_1 \ldots Y'_N \) and \( T' \). When solving this system of equations for detailed chemical mechanisms with many chemical reactions and many different species a big calculation effort has to be done. Numerical methods can be applied to solve the system of equations.

From this first analytical analysis we can see that the reactor temperature depends amongst others on the mass flow rate, the participating components in the reaction and their mass fractions, possible cooling systems (represented by \( \dot{Q}_K \)) as well as from the inlet temperature.

Qualitative analysis of the reactor working behaviour
For a qualitative analysis of the reactor behaviour the model has to be simplified. The system is assumed to have a global reaction with one reaction step:

\[ F + \gamma \dot{Q}_x \rightarrow P \]  

(4)

The reaction rate is specified as follows, with \( A_0 \) and \( \dot{E}_A \) as experimental parameters:
\[ k = A \cdot C_p \cdot C'_{\text{qs}} \cdot \exp\left(-\frac{E_A}{RT'}\right) \]  (5)

If we assume an approximately constant heat capacity \( C_p = \sum_{i=1}^{n} (Y_{A_i} \cdot C_{p,A_i}) \approx \text{const.} \), then we will have a system of equations with two equations and two unknowns (\( T' \) and \( Y'_F \)).

\[ M \cdot (Y_F - Y'_F) = k \cdot W_F \cdot V \]  (6)
\[ c_p \cdot (T' - T_0) = H_u \cdot (Y_F - Y'_F) \]  (7)

If we combine these two equations we get the following expression, where the left side represents the sensible heat abstraction per second through the mass flow rate and the right side the heat release rate through the chemical reaction.

\[ \frac{\dot{M}}{V} \cdot c_p \cdot (T' - T_0) = H_u \cdot k \cdot W_B \]  (8)

Figure 2: Graphical representation of the balance between heat release (blue) and heat removal (black).[4]

As we can see from Figure 2 the heat release depending on the reaction rate \( k \) which is proportional to \( \exp(\cdot E_A/RT) \) increases with \( T' \). Because of the decrease of the mass fraction of the reactants (fuel and oxygen) after the reaction, after a certain temperature \( T_x \), the reaction rate decreases and with it the heat release. For the contrary the heat removal is linearly proportional to \( T' \), as shown in equation 8.

Three different working conditions can be abstracted from this diagram. In cold working conditions (K) the inlet and outlet temperatures are almost the same and almost no chemical reaction is observed, as the minimal temperature for the chemical reaction to start is not achieved. In hot working conditions (H) the temperature at the outlet approaches the adiabatic flame temperature \( T_{ad} \) which represents the case for no heat exchange and hence, 0 mass flux. An intermediate situation (I) can be found. This last working point is very unstable and is not found in the reality.

The limits of the heat flux are marked with the points \( X \) and \( Z \). For higher mass flow rate than in case \( X \) the amount of removed heat is too high and the reaction is quenched. The minimal mass flow rate is marked with \( Z \). Below this mass flow rate the reactor can only be run in hot conditions, as can be seen from Figure 3. In this case auto-ignition occurs. Thus, the reactor conditions are only stable in the upper part from the curve in Fig. 3 before the conditions in point \( X \) are reached. After reaching that point only unstable conditions till the quenching of the reaction will follow.

Figure 3: Working conditions of an exothermic reactor[4]

This limit of the working conditions of the reactor is called self-extinguishing limit. This limit can be calculated approximately after introducing the parameters \( \phi \), the fuel-air ratio \( \phi \) and \( A' \):

\[ \phi = \frac{Y_F - Y'_F}{Y_F} = \frac{T' - T_0}{T_{ad} - T_0} \]  (10)
\[ \phi = \frac{W_{Ox}}{W_F} \cdot Y_F \]  (11)
\[ A' = A \cdot \left(\frac{Y_{Ox}}{W_{Ox}}\right)^\gamma \cdot \left(\frac{W}{R}\right)^n \]  (12)

After inserting these parameters in eq. 8 and after some reformulations, we obtain:

\[ \frac{\dot{M}}{V \cdot p} = A' \cdot \frac{1}{T^n} \cdot (1 - \phi) \cdot (1 - \phi_\phi)^{n-1} \cdot \exp\left(-\frac{E_A}{RT}\right) \]  (13)

The left side of eq. 13 is called the reactor load and the right side represents the reaction rate. To calculate the temperature for the maximal reaction rate, the equation can be derived after \( T' \) and equalized to 0.

For the stoichiometric case with \( \phi = 1 \)
we obtain the following derivative for the right side of the equation:

\[
\frac{d}{dT'} \left[ \left( 1 - \frac{T_{ad}}{T'} \right)^{n} \exp \left( -\frac{E_A}{RT'} \right) \right] = 0
\]  

(15)

\[
T' \approx T_{ad} \cdot \left( \frac{1}{1 + \frac{n \cdot R \cdot T_{ad}}{E_A}} \right)
\]

(16)

For big activation energy values \( E_A (E_A/R \approx 10^6\text{K}) \) for combustion of hydrocarbons), we can use the approximation \(1/(x+1) \approx 1-x \) for small \( x \).

\[
T_x \approx T_{ad} \approx T_{ad} \cdot \left( 1 - \frac{n \cdot R \cdot T_{ad}}{E_A} \right)
\]

(17)

As it can also be seen from Fig. 2 the self-extinguishing temperature will be close to the adiabatic temperature. The maximal load and hence the maximal mass flow rate can then be approximated from eq. 13, 14 and 17 for big \( E_A \) values. The following relation is found:

\[
\frac{M_x}{V' p^n} \approx A' \cdot \left( \frac{R T_{ad}}{E_A (T_{ad} - T_c)} \right)^{n} \cdot \exp \left( -\frac{E_A}{RT} \right)
\]

(18)

CONCLUSIONS

After an analytical analysis of the species and energy balance we see that the stable working conditions of an exothermic reactor are very limited. If the working limits are exceeded uncontrolled unstable conditions develop till the reaction is quenched. The stable working conditions depend mainly on the reactor temperature and the mass flow rate. For mass flow rates bigger than \( M_x \) no stable conditions are possible. An approximate calculation of this value is given through eq. 18, as well as for the in that case existing reactor temperature with eq. 17.

Other parameters that influence the reactor temperature appear to be the inlet temperature, the reacting components and their composition as well as the cooling systems. This last one includes the wall capacitance, high wall capacitance increases the working stability, as well as the appropriate cross-section variations, with reduced diameters at the hot spot improving the heat transport at those regions.

For more accurate analysis of the real dependence of reaction rate and the temperature a numerical solving of the problem should be carried out.

REFERENCES


